# Oxygen-18 dynamics in precipitation and streamflow in a semi-arid agricultural watershed, Eastern Washington, USA

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Abstract:

Understanding flow pathways and mechanisms that generate streamflow is important to understanding agrochemical contamination in surface waters in agricultural watersheds. Two environmental tracers, $\delta^{18}O$ and electrical conductivity (EC), were monitored in tile drainage (draining 12 ha) and stream water (draining nested catchments of 6-5700 ha) from 2000 to 2008 in the semi-arid agricultural Missouri Flat Creek (MFC) watershed, near Pullman Washington, USA. Tile drainage and streamflow generated in the watershed were found to have baseline $\delta^{18}O$ value of $-14 \cdot 7‰$ (VSMOW) year round. Winter precipitation accounted for 67% of total annual precipitation and was found to dominate streamflow, tile drainage, and groundwater recharge. 'Old' and 'new' water partitioning in streamflow were not identifiable using $\delta^{18}O$, but seasonal shifts of nitrate-corrected EC suggest that deep soil pathways primarily generated summer streamflow (mean EC 250 µS/cm) while shallow soil pathways dominated streamflow generation during winter (EC declining as low as 100 µS/cm). Using summer isotopic and EC excursions from tile drainage in larger catchment (4700-5700 ha) stream waters, summer in-stream evaporation fractions were estimated to be from 20% to 40%, with the greatest evaporation occurring from August to October. Seasonal watershed and environmental tracer dynamics in the MFC watershed appeared to be similar to those at larger watershed scales in the Palouse River basin. A 0·9‰ enrichment, in shallow groundwater drained to streams (tile drainage and soil seepage), of $\delta^{18}O$ values from 2000 to 2008 may be evidence of altered precipitation conditions due to the Pacific Decadal Oscillation (PDO) in the Inland Northwest. Copyright © 2009 John Wiley & Sons, Ltd.

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## INTRODUCTION

Stable isotope ratios of water ($^2H$ and $^{18}O$) have been useful tools in watershed studies over the past 40 years, and have helped hydrologists gain insight into soil and surface water dynamics within watersheds (Zimmermann *et al.*, 1967; Gat and Levy, 1978; Gat and Gonfiantini, 1981; Barnes and Allison, 1983, 1984, 1988; Gibson *et al.*, 1993, 1998, 2000, 2002, 2005; Gat, 1996; Kendall and McDonnell, 1998; Gibson, 2001, 2002). By combining stable isotope hydrology with hydrochemistry, a better understanding of the hydrologic processes that shape intra-watershed dynamics can be achieved (Hooper *et al.*, 1990; Shanley *et al.*, 2002).

Understanding the isotope hydrology of managed agricultural ecosystems could contribute to (i) development of fate and transport models to understand surface and ground water contamination as a result of agricultural practices, (ii) the implementation of environmentally-sound artificial tile drainage systems, and thus (iii)

optimizing productivity while minimizing environmental impacts. Tile-drained catchments generate significant agrochemical pollution in surface waterways in some areas of the United States (Kladivko *et al.*, 1991; Randall *et al.*, 1997; Cambardella *et al.*, 1999). Therefore it is vital to understand how pedologic and hydrologic setting influences the surface and subsurface transport pathways of these chemicals.

Numerous studies have investigated intra-watershed dynamics during precipitation events using isotopic and geochemical compositions observed at different reaches of small watersheds. This research has been conducted in various climatic conditions, including humid and temperate forested catchments (Hooper and Shoemaker, 1986; Hooper *et al.*, 1990; Genereux *et al.*, 2002, 2004, 2006; Peters and Ratcliffe, 1998; Gburek and Folmer, 1999; Gibson *et al.*, 2000; Endreny, 2002; Shanley *et al.*, 2002), alpine or northern latitude catchments (Gibson *et al.*, 1993; Laudon and Slaymaker, 1997; Carey and Quinton, 2005; Kvaerner and Klove, 2006, 2008), and coastal semi-arid catchments in Australia (Barnes and Allison, 1983, 1984, 1988; Walker and Brunel, 1990; Marimuthu *et al.*, 2005, Gibson *et al.*, 2008), and other

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semi-arid cathments (Strauch *et al.*, 2006), or it has been aimed at identifying spring source and precipitation contribution to groundwater in arid climates (Winograd *et al.*, 1998).

Stable isotope ratios have been applied to storm hydrograph separation (Sklash *et al.*, 1976; Sklash and Farvolden, 1979), and can identify 'old' and 'new' water (pre-event and event waters, Genereux and Hooper, 1998) contributions to streamflow during events. On the other hand, electrical conductivity (EC) can identify hydrologic pathways, based on local geology and mineral-water interaction time, where higher EC implies long and deep subsurface pathways and lower EC implies short and shallow subsurface pathways (Freeze and Cherry, 1979). Hooper and Shoemaker (1986) at the Hubbard Brook Experimental Forest in New Hampshire, and Shanley *et al.* (2002) at the Sleepers River Research Watershed in Vermont, both used geochemical and stable isotope data to create hydrograph separations to identify 'old' and 'new' water contributions to stream flow during storm events and spring snowmelt. Both studies observed $\delta D$ and $\delta^{18}O$ values that were high during the winter and low in April as snow pack (low isotopic values relative to rain) melted and increased discharge from the watersheds. They also found, like their predecessors (Sklash and Farvolden, 1979), that baseflow actually contributed a substantial amount of water to streamflow generation even during storm events. Genereux *et al.* (2002, 2004, 2006) identified sources of groundwater discharge to surface water using both geochemical and stable isotope data in a small lowland watershed in Costa Rica. Isotopic variation in precipitation was not large (mean $\delta^{18}O$ was $-3.4‰$ (VSMOW), SD $2.04‰$), but was slightly seasonal. They also found that isotopic data are sometimes unreliable due to temporal variability in $\delta^{18}O$ values within sites and additional environmental tracer data were needed to perform water budget calculations.

The Palouse region in eastern Washington offers a unique opportunity to investigate catchment-to-basin scale hydrologic dynamics in a rain-fed semi-arid agricultural watershed. This region is typical of many water-stressed parts of the world where groundwater exploitation is greater than recharge to the regional aquifer. Long-term water level declines and concern for the sustainability of the Grande Ronde aquifer has lead to a number of studies regarding regional aquifer recharge (Lum *et al.*, 1990; Larson *et al.*, 2000; O'Geen *et al.*, 2005; Douglas *et al.*, 2007) that have only briefly characterized surface hydrology. This fact leads to the need to evaluate surface and shallow groundwater (Wanapum aquifer) as possible future water resources. As a result, understanding surface flow pathways and water quality is essential.

The goal of this research was to investigate the behavior of oxygen isotopes in precipitation, soil water, and stream water over a period of 7 years to identify the sources and mechanisms of streamflow generation, and trace the seasonal isotopic evolution of stream waters, in the Missouri Flat Creek (MFC) watershed in eastern Washington State. The specific objectives

were to (i) characterize seasonal watershed response to precipitation inputs using stable isotope systematics and EC of surface and soil waters, (ii) characterize the isotopic evolution of $\delta^{18}O$ values in surface waters from catchment-to-basin watershed scales ranging from monthly to annual time scales, (iii) estimate evaporative flux from stream waters in summer using both stable isotope and EC mass balances, and (iv) test previous models of infiltration and streamflow generation in the MFC watershed.

## METHODS

### Site description and sampling locations

Research was performed within the MFC watershed ($46°46'44''$N, $117°05'19''$W), located in the Palouse River Basin, north of Pullman, Washington, in the semi-arid area of the Palouse in eastern Washington and northern Idaho (Figure 1). Annual precipitation in the area ranges between $31–58$ cm $y^{-1}$ (Donaldson *et al.*, 1980), with the majority of precipitation occurring in winter. Mean temperatures ranged from $27°C$ in the summer to $-7°C$ in the winter (Geyer *et al.*, 1992). Rain-fed cultivation agriculture dominates the region and crops consist mostly of grains and lentils, which are rotated. The area's topography is characterized by rolling hills (up to 50 m of local relief) of deflation loess deposits overlying Columbia River Basalt flows (McDonald and Busacca, 1992). Soils in the region are silt loam Mollisols, which have been mapped as part of the Palouse-Thatuna Association soil series (USDA, 1978). Subsurface lateral flow components make important contributions to streamflow, particularly during periods of high precipitation after soil wetting has occurred (Mallawatantri *et al.*, 1996; Brooks *et al.*, 2006; Keller *et al.*, 2008). As is common in areas of poor drainage, low-lying areas are artificially drained with 'tile' drains (perforated PVC pipe that is buried horizontally in the ground), which act as linear sinks for shallow groundwater during periods of high precipitation, short-circuiting slower lateral drainage pathways to streams. Perched water tables are common in this area of eastern Washington due to widespread occurrence of hydrologically restrictive horizons, fragipans, and argillic horizons (O'Geen *et al.*, 2005). The tile-drained proportion of the total study area is unknown.

Hydrologic monitoring was performed from October 2000 to February 2008, at six locations within the MFC watershed, which corresponded to the outlets of five nested catchments (Figure 1), and sampling was conducted at least bimonthly, and more frequently during periods of high precipitation. Locations ES-6 and ES-106 on the Cook Agronomy Farm (CAF), a no-till experimental farm operated by the US Department of Agriculture-Agricultural Research Service (USDA-ARS), were an ephemeral rill and a stream draining approximately 6 ha and 106 ha, respectively, and flowed episodically during winter after precipitation events or periods of snowmelt. TD-12 was a tile drain outflow draining approximately
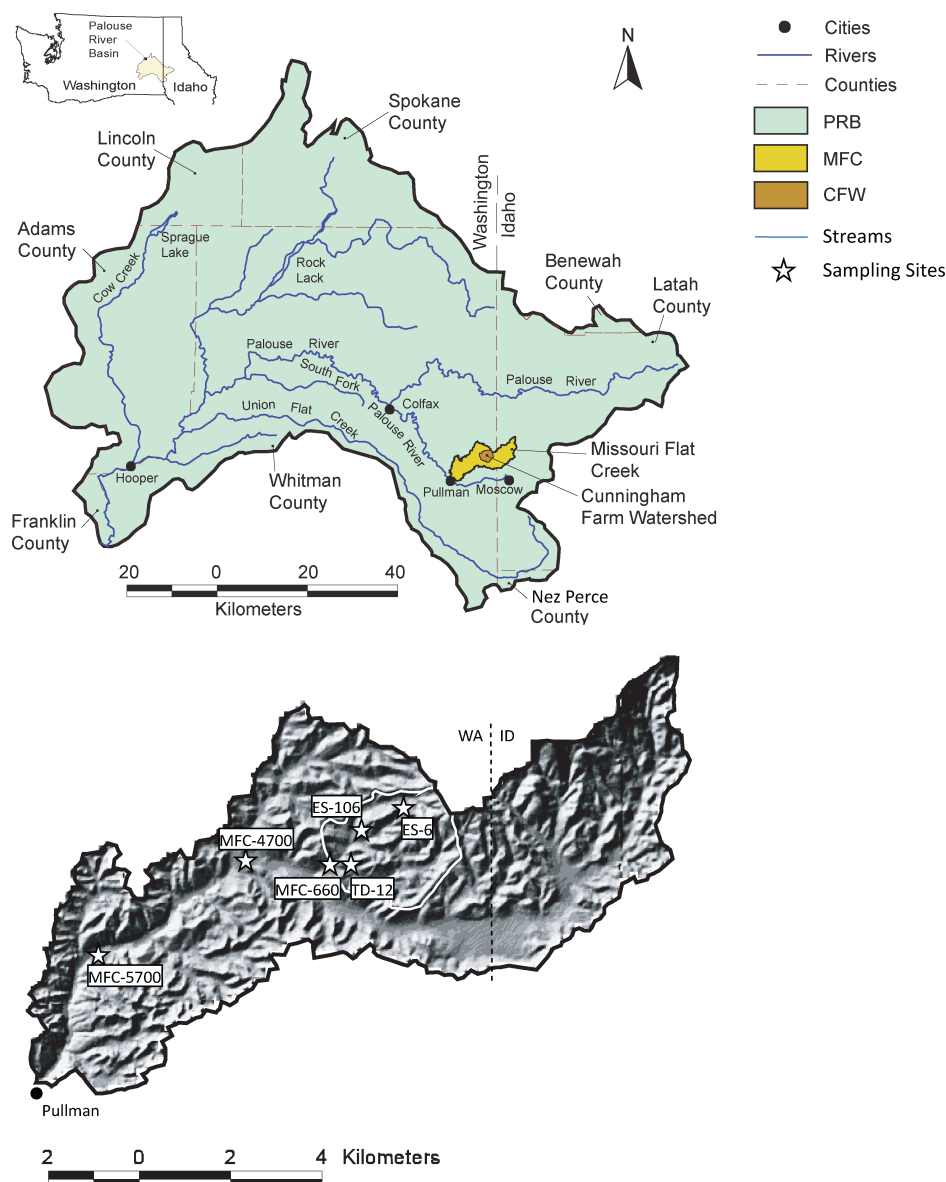
Figure 1. Digital elevation model of the MFC watershed (lower panel) (6000 ha), which drains to the South Fork of the Palouse River and is tributary to the Palouse River (upper panel) (draining 647 500 ha). MFC catchment sampling locations and areas (ha) are shown by stars. TD is tile drain and ES is ephemeral stream (Modified from Abdou, 2003)

12 ha at the southwest corner of CAF (Keller *et al*., 2008) and was only dry in August. MFC-660 was a ditch draining 660 ha consisting of tile and non-tile drained fields, and flowed throughout the year. Tension and zero-tension lysimeters, installed in a trench at depths of 20, 65, and 90 cm 10 m north of the TD-12, were sampled regularly until a large flooding event pulled the tubing from the lysimeter cups in 2006. MFC-4700 and MFC-5700 were ephemeral streams draining approximately 4700 ha and 5700 ha, respectively, of the MFC watershed. Surface water levels at MFC-660 and MFC-4700 were measured every hour with a Global Logger® pressure transducer and gauged using the Manning equation to calculate discharge in mm day$^{-1}$. Discharge at TD-12 was periodically measured in triplicate with a bucket and stopwatch and converted to mm day$^{-1}$. Daily discharges and precipitation were summed and runoff ratios

were calculated on a yearly basis. Volumetric soil water content was measured at four depths (25–85 cm) by time domain reflectometers (TDR) installed at TD-12.

*Sample collection and lab preparation*

Field collection methods for waters were designed to be consistent with US Geological Survey (USGS) sampling methods (Shelton, 1994). All samples and field blanks were collected in 250 ml HCl acid-washed Nalgene® bottles. EC and temperature were measured using a temperature compensated EC probe (model 115, Orion/ThermoFisher Scientific). Samples were then vacuum filtered through Whatman® 0·45 μm cellulose nitrate membrane filters, transferred to acid-washed scintillation vials, and stored in a dark cabinet at room temperature for $\delta^{18}O$ analyses.

The oxygen isotope composition of waters was measured using a continuous-flow gas chromatograph (GC)

(GasBench II, Thermo Finnigan) mass spectrometer (Delta S, Thermo Finnigan) located in the GeoAnalytical Lab in the School of Earth and Environmental Sciences (SEES) at Washington State University (WSU). Out of each sample 500 μl was pipetted into a sodaglass Exetainer® (product code 738 W, Labco Limited) and tightly fitted with a septum. Samples were then placed in a temperature-controlled tray set at 32 °C. Equilibrated headspace $CO_2$ (Epstein and Mayeda, 1953) was then transported via an inert He carrier through the GC and to the Faraday detectors measuring atomic masses 44, 45, and 46. Gas Bench $\delta^{18}O$ analytical uncertainty was $\pm 0.28‰$ and method uncertainty, due to storage issues prior to 2004, was conservatively estimated to be $\pm 0.58‰$ (Goodwin, 2006). Raw $\delta^{18}O$ values were first temperature corrected following Bottinga and Craig (1969) and Bottinga and Javoy (1973) and then corrected according to known isotopic standards VSMOW ($\delta^{18}O = 0.0‰$), GISP ($\delta^{18}O = -24.78‰$), SLAP ($\delta^{18}O = -55.5‰$), and three internal standards: WAWA 1 ($\delta^{18}O = -16.48‰$), WAWA 2 ($\delta^{18}O = -16.67‰$), and DIWA ($\delta^{18}O = -18.87‰$) (Goodwin, 2006). Measured $^{18}O/^{16}O$ ratios were reported as $\delta^{18}O$ with units of ‰ (per mil) relative to VSMOW.

Precipitation amounts were monitored from October 2000 to December 2007 and bulk samples were collected bimonthly in acid-washed 1000 ml Nalgene® bottles, which were placed beneath a tipping-bucket at TD-12. Meteorological data were collected at ES-6 up to January 2006. Due to vandalism to the rain collector at ES-6, meteoric data after January 2006 was used from the Smokey Air Data (SAD) website published by the WSU College of Engineering as part of their environmental measurements course (http://smokey.ce.wsu.edu/airdata/Met_Data/, accessed April 2008). Precipitation $\delta^{18}O$ data were both monthly and seasonally volume weighted.

*Estimation of surface water evaporation based on $\delta^{18}O$ and EC*

The Craig-Gordon model (Craig and Gordon, 1965) as modified by Gibson *et al.* (1993) was used to estimate the summer evaporative flux based on isotopic fractionation of surface waters at MFC-4700 and MFC-5700. The Craig-Gordon model of the evaporative flux, $\delta_E$, in delta form is defined as

$$\delta_E = \frac{\alpha^* \delta_L - h\delta_a - \varepsilon^* - \Delta\varepsilon}{(1-h) + \Delta\varepsilon/10^3} \approx \frac{\delta_L - h\delta_a - \varepsilon^* - \Delta\varepsilon}{(1-h)} \quad (1)$$

where

$$\varepsilon^* = (1 - \alpha^*) \cdot 10^3 \quad (2)$$

$$\Delta\varepsilon = (1-h) \cdot \theta \cdot n \cdot C_D \cdot 10^3 \quad (3)$$

$$C_D = 28.515‰$$

$$\theta = 1$$

$$n = 0.5 \quad (4)$$

$h$ is the relative humidity (0 to 1), $\delta_a$ is the isotopic composition of atmospheric water vapor, $\delta_L$ is the liquid water isotopic composition, $\theta$ is the weighting factor which is 1 for small surface water evaporation that does not induce an increase in relative humidity, and $n$ is an empirical term that is 0.5 for an open water body under natural conditions. Detailed description and derivation of the Craig-Gordon model are provided in Gat (1996).

The Craig-Gordon model was modified by Gibson *et al.* (1993) in order to estimate the evaporation-to-input fraction ($E/I$) for two lakes in northern Canada. This isotopic mass balance approach utilized the equilibrium fractionation factor for liquid water-to-water vapor ($\Delta_{L-V}$) established by Horita and Wesolowski (1994):

$$10^3 \ln \alpha_{L-V} \approx \Delta_{L-V} = \delta^{18}O_L - \delta^{18}O_V \quad (5)$$

$$\Delta_{L-V} \approx -7.685 + 6.7123 \left(\frac{10^3}{T}\right)$$
$$- 1.6664 \left(\frac{10^6}{T^2}\right) + 0.35041 \left(\frac{10^9}{T^3}\right) \quad (6)$$

$$\delta^{18}O_V = \delta^{18}O_L - \Delta_{L-V} \quad (7)$$

where $\delta^{18}O_V$ is the estimated isotopic composition of water vapor, $\delta^{18}O_L$ is the isotopic composition of the evaporated liquid, and $T$ is the average temperature in Kelvin for the entire study period (8.38 °C = 281.53 K) for the MFC watershed.

Gibson *et al.* (1993) used an approximate value for $\delta^{18}O_V$ (Equation 7) and measured $\delta^{18}O_L$ to estimate the limiting isotopic enrichment ($\delta^*$), where $\delta^*$ is defined as follows:

$$\delta^* = \frac{h\delta^{18}O_V + \Delta_{L-V}}{h - \Delta_{L-V}} \quad (8)$$

and

$$E/I_{^{18}O} = \frac{1-h}{h} \cdot \frac{\delta^{18}O_L - \delta^{18}O_P}{\delta^* - \delta^{18}O_L} \quad (9)$$

$E/I_{^{18}O}$ is the evaporation-to-input fraction, and $\delta^{18}O_P$ is the isotopic composition of the source water (precipitation $\delta^{18}O$ for Gibson *et al.*, 1993; TD-12 $\delta^{18}O$ from summer drainage for MFC). Evaporative isotopic fractionation is dependent on the relative humidity and decreases as relative humidity increases until isotopic equilibrium is met at 100% humidity (Craig, 1961). Monitored temperature ranges in MFC did not vary considerably, which reduced $\delta^*$ (and therefore $E/I_{^{18}O}$) dependency on $\Delta_{L-V}$ and increased $\delta^*$ dependency on humidity and $\delta^{18}O_V$ (Horita and Wesolowski, 1994). An average relative humidity of 0.384 was estimated based on humidity data collected by the WSU College of Engineering from 2005 to 2007 in addition to estimates of relative humidity from other vadose zone evaporation studies in the region (DePaolo *et al.*, 2004). For summer, $\delta^{18}O$ values were higher than the estimated $\delta^*$, and calculated $E/I_{^{18}O}$ fractions were greater than 1 (Aug–Oct); for this reason, MFC-4700 $\delta^{18}O$ values were averaged over the entire summer.
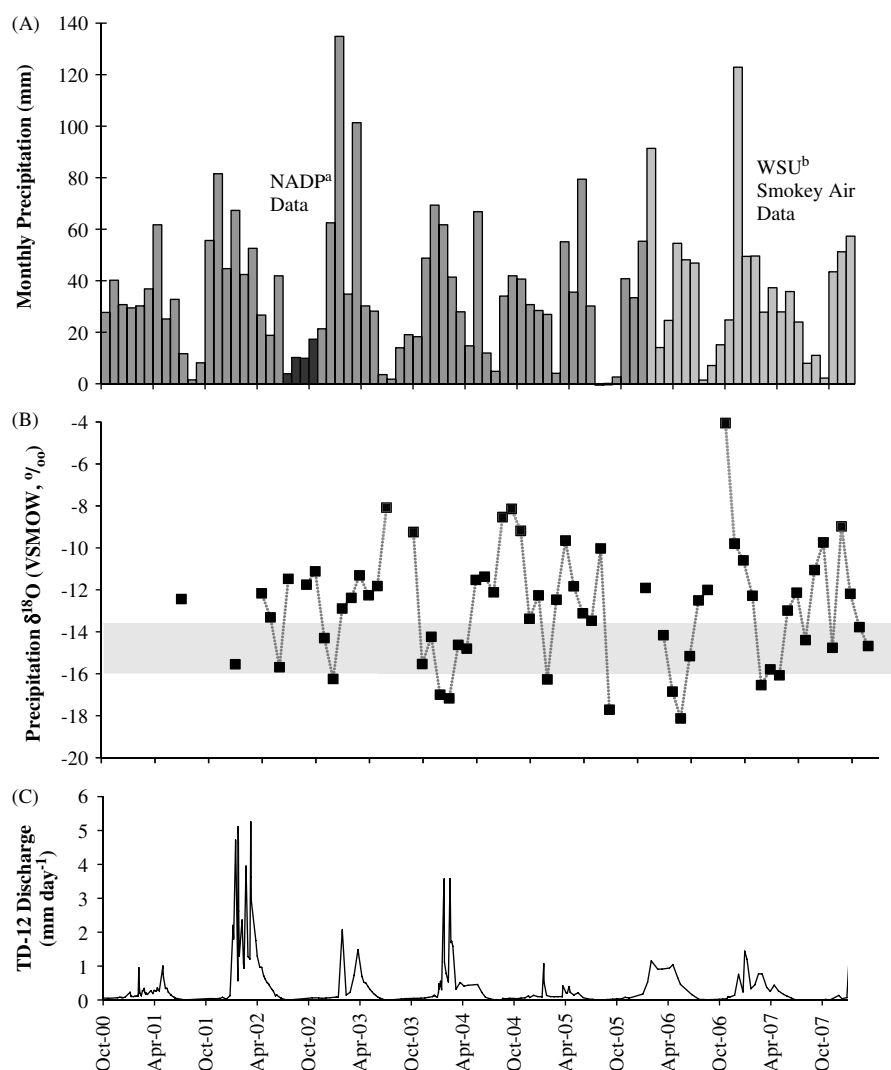
Figure 2. Precipitation amounts are monthly (A), precipitation $\delta^{18}$O (VSMOW, ‰) was monthly volume weighted (B), and discharge was measured at TD-12 (C). Mean TD-12 $\delta^{18}$O was −14·7‰ (SD 0·92‰) represented by gray bar in panel B. Precipitation $\delta^{18}$O was generally higher during summer and lower during winter; ∼67% of annual precipitation fell between October and April. The superscript letters ([a,b]) denote periods of meteorological data logger malfunction were supplemented with National Atmospheric Deposition Data (NADP) and WSU Smokey Air Data

Independent estimates of seasonal evaporation were obtained via simple mass balance using:

$$E/I_{EC} = \frac{(EC_{Surfacewater} - EC_{TD-12})}{EC_{Surfacewater}} \quad (10)$$

where $EC_{Surfacewater}$ is the average nitrate-corrected EC over the entire summer (MFC-4700) or the average nitrate-corrected EC from August-October (MFC-5700), $EC_{TD-12}$ is the average nitrate-corrected EC from TD-12 discharge over the same time periods for MFC-4700 and MFC-5700, and $E/I_{EC}$ is the evaporation-to-input fraction, in this case based on EC enrichment instead of $\delta^{18}$O enrichment.

## RESULTS

*Precipitation and streamflow generation in the MFC watershed*

Precipitation in the region originates from westerly storm fronts that move into eastern Washington from the Pacific moving over the Cascade Mountain Range (Takeuchi *et al.*, 2009). Over the study interval, an average of 67% of annual precipitation fell between October and April. Winter precipitation took the form of snow during the coldest parts of the wet season between November and February where mean monthly temperatures were below 0 °C. Typically, snow pack was intermittent during winter as warm weather usually melted snow between events. Late winter precipitation was usually in the form of rain and was regional in nature. Summer precipitation was usually in the form of short, isolated thunderstorms, and overland flow (during summer or winter) was not observed or measured during this study (Keller *et al.*, 2008).

Discharges at TD-12, MFC-660, and MFC-4700 (lower panels, Figures 2–4, respectively) were large in the winter, beginning typically in January-February after approximately 150 mm of precipitation early in the water year, which increases the soil water content in the upper 1 m of the soil profile (Keller *et al.*, 2008).
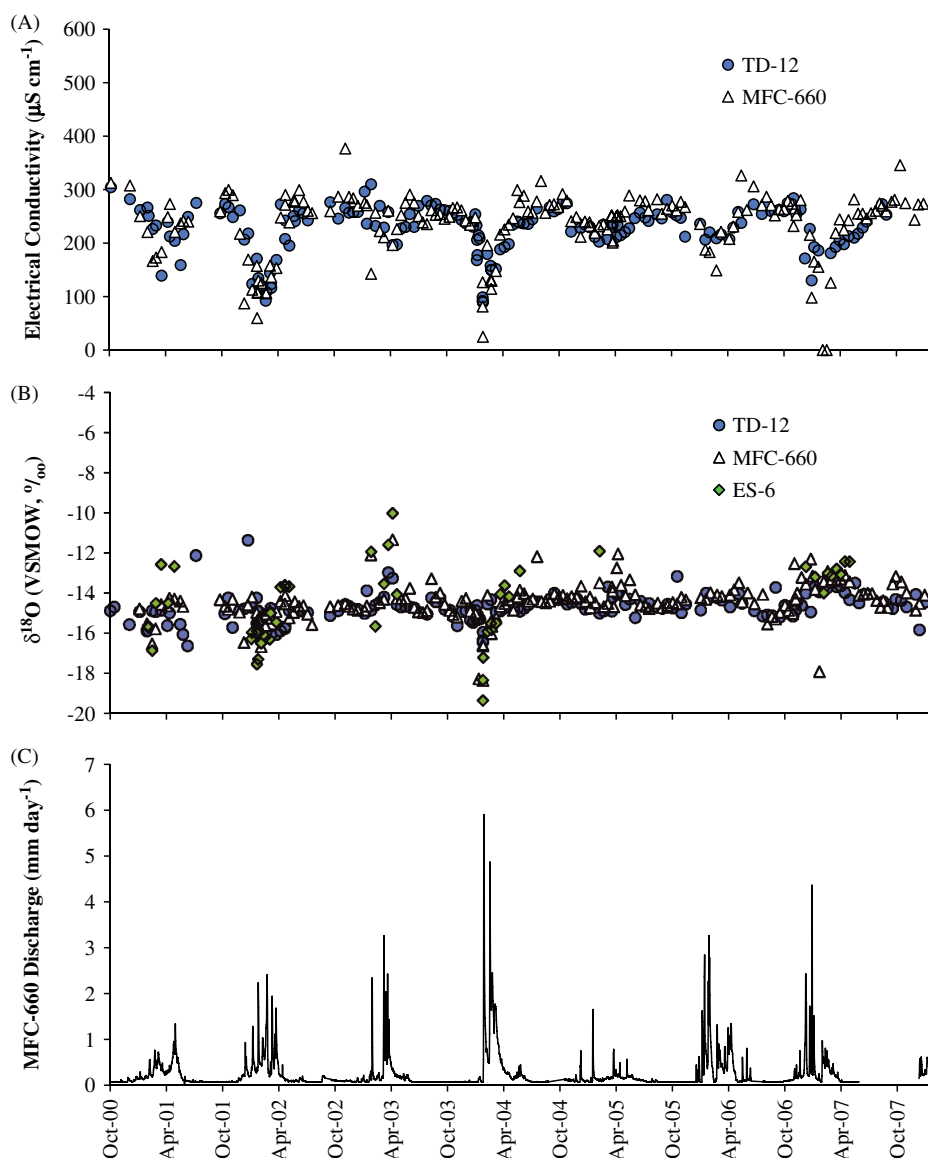
Figure 3. EC (A), $\delta^{18}$O (B), and discharge (C) at small catchment scales (6 to 660ha). Sharp isotope excursions in ES-6 (e.g. January, 2004), which were driven by precipitation or melting events, were dampened in MFC-660 and barely evident in TD-12. $\delta^{18}$O analytical error was 0·58‰

Summer discharges at all sites in the watershed dropped dramatically as soil water content decreased after the onset of spring crop growth, and rainfall was intercepted by plants rather than feeding deep percolation. Discharge at TD-12, MFC-660, or MFC-4700 ceased during some years toward the end of summer.

Alfalfa (*Medicago sativa*) was planted in the spring of 2006 and consisted of a 20 m strip abutting the drainage ditch and running north from the TD-12 outlet. Alfalfa is a deep-rooted perennial that is often used as a hydrologic barrier of subsurface drainage to edge of field ditches. The alfalfa did not apparently affect TD-12 discharge for the water year 2006–2007.

Peak winter discharge fluxes (mm day$^{-1}$) observed at MFC-660 and MFC-4700 had similar values and were synchronous to TD-12 peak discharge flux. Summer discharges at MFC-4700 decreased as summer progressed until harvest in August. During some years, MFC-5700 and MFC-4700 became dry at the end of July.

Runoff ratios (discharge flux/precipitation flux) were calculated for TD-12 and MFC-660 (Table I). Years with low runoff ratios corresponded to years with below normal precipitation. Runoff ratios for the MFC ranged between 0·1 and 0·4 with an average of 0·2. For this study, discharge measured at MFC-660 was probably the most accurate because TD-12 discharge was gauged manually when sampling rather than hourly, and MFC-4700 stream morphology changed during the study due to increased sediment. A data logger malfunction occurred from July to September 2007 at MFC-660, but flow was minimal at this time and this malfunction did not cause significant error in runoff ratio calculations for that year. Runoff ratios were calculated for available USGS historical data (Williams and Pearson, 1985) at the MFC outlet (nearly equivalent to MFC-5700), South Fork of the Palouse River at Pullman (34 200 ha), and Palouse River at Hooper (647 500 ha) (Table II). Runoff ratios at these larger scales were similar over the different
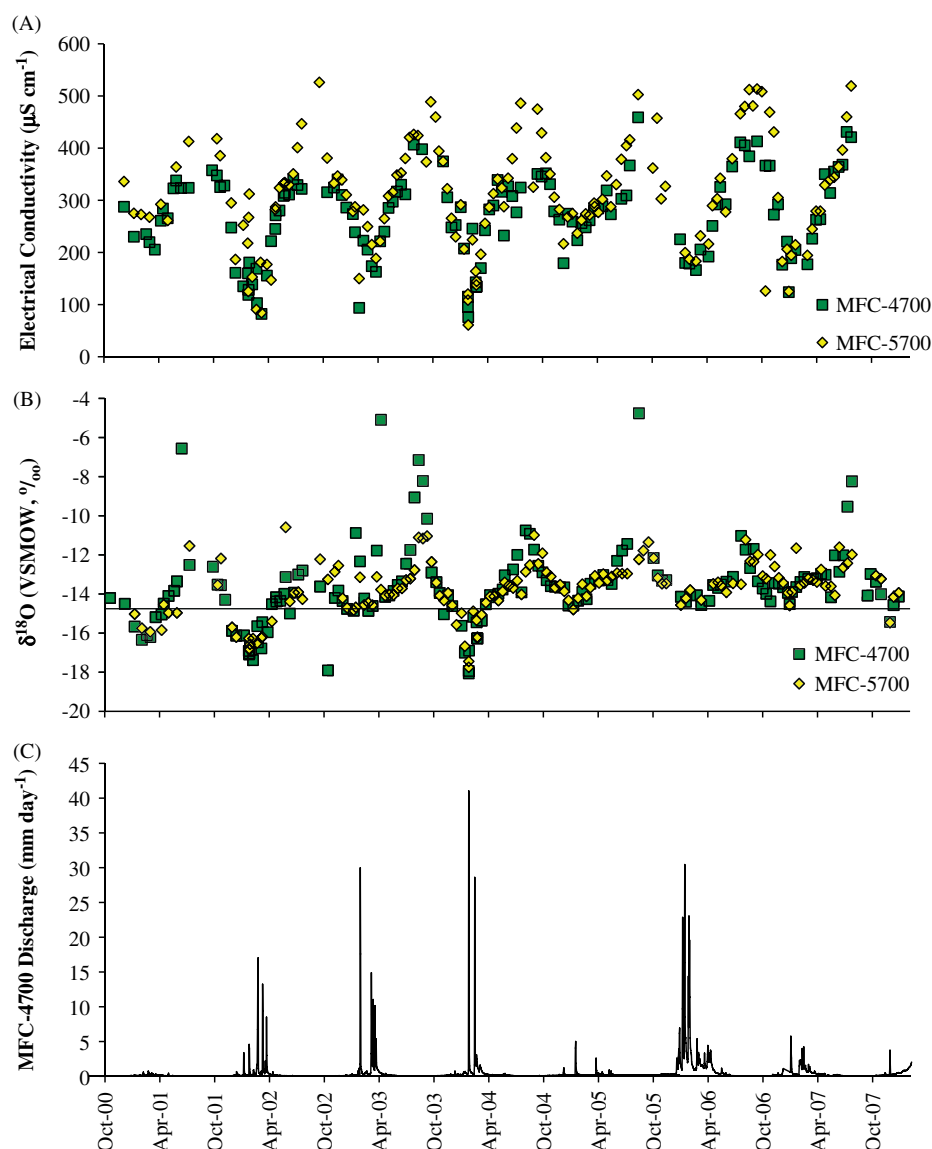
Figure 4. EC (A), $\delta^{18}O$ (B), and discharge (C) at large catchment scales (4700–5700 ha). Sinusoidal $\delta^{18}O$ seasonality coincides with EC seasonality and is driven by evaporation of the surface water. Black horizontal line in panel B is the average $\delta^{18}O$ baseline value at TD-12 ($-14\cdot7‰$, SD $0\cdot92‰$) over the course of the study

averaging periods and were around $0\cdot2$, which were similar to runoff ratios calculated at TD-12, and MFC-660 for most years of this study.

*Stable isotopes of MFC waters*

On the Palouse, monthly volume-weighted winter precipitation $\delta^{18}O$ values ranged from $-18‰$ to $-12‰$, while summer months had $\delta^{18}O$ values ranging from $-11‰$ to $-4‰$ (Table I, Figure 2). In general, monthly volume-weighted winter precipitation samples (Figure 2) showed lower $\delta^{18}O$ values than summer precipitation. Variability in $\delta^{18}O$ values of winter precipitation can be attributed to a combination of temperature and source area effects (in this case, latitude effect with storm front origin of British Columbia vs California).

The grand mean of all observed TD-12 and MFC-660 $\delta^{18}O$ values (Table II; Figure 3) was $-14\cdot7‰$, SD $0\cdot93‰$. Three sharp $^{18}O$ depletion events occurred in March 2002, January 2004, and December 2007 where TD-12 $\delta^{18}O$ values were $-16\cdot1‰$, $-16\cdot4‰$, and $-15\cdot8‰$, respectively. MFC-660 waters were even more $^{18}O$ depleted at these times and closely matched $\delta^{18}O$ values from ES-6 (Figure 3). These events coincided with very low EC. Two abnormal $^{18}O$ enrichment peak events occurred in March 2003 and February to March 2007 with TD-12 $\delta^{18}O$ values of $-13\cdot0‰$ and $-13\cdot6‰$, respectively, which coincided with highly $^{18}O$ enriched winter precipitation and overland flow at ES-6. Excursions observed during the first year of this study were due to sample storage issues (Goodwin, 2006) and were ignored.

MFC-4700 and MFC-5700 $\delta^{18}O$ values responded rhythmically and consistently from summer to winter (Figure 4). Summer $\delta^{18}O$ values exhibited enrichment that consistently peaked at $-11‰$ and $-11\cdot9‰$ in July and August for MFC-4700 and MFC-5700, respectively. Four extreme $^{18}O$ enrichment events at MFC-4700, which

Table I.

| Season/year (October-March: winter) (April-September: summer) | Total seasonal precipitation (mm) | Seasonal-volume weighted $O^{18}O$ (‰) | Total water-year precipitation (mm) | Yearly discharge fux TD-12 (mm/year) | Yearly discharge flux MFC-660 (mm/year) | Yearly runoff ratio (TD-12/PPT) | Yearly runoff ratio (MFC-660/PPT) |
|---|---|---|---|---|---|---|---|
| **Winter 2000–2001** | 195 | No data | 336 | 78 | 69 | 0.23 | 0.21 |
| **Summer 2001** | 141 | −12.4 | | | | | |
| **Winter 2001–2002** | 344 | −15.6 | 456 | —[a] | 95 | —[a] | 0.21 |
| **Summer 2002** | 111 | −13.8 | | | | | |
| **Winter 2002–2003** | 372 | −13.0 | 469 | 106 | 68 | 0.23 | 0.15 |
| **Summer 2003** | 97 | −11.2 | | | | | |
| **Winter 2003–2004** | 267 | −15.8 | 442 | 212 | 123 | 0.48 | 0.28 |
| **Summer 2004** | 174 | −10.2 | | | | | |
| **Winter 2004–2005** | 186 | −13.0 | 334 | 57 | 46 | 0.17 | 0.14 |
| **Summer 2005** | 148 | −12.7 | | | | | |
| **Winter 2005–2006** | 260 | −14.5 | 433 | 138 | 100 | 0.32 | 0.23 |
| **Summer 2006** | 173 | −12.6 | | | | | |
| **Winter 2006–2007** | 312 | −13.7 | 421 | 102 | 68[b] | 0.24 | 0.16[b] |
| **Summer 2007** | 109 | −12.7 | | | | | |
| **Winter Mean** | 277 | −14.3 | | | | | |
| **Summer Mean** | 136 | −12.2 | | | | | |

Winter and summer seasonal precipitation $O^{18}O$ values from 2000 to 2007 were volume weighted. All $O^{18}O$ values are relative to VSMOW. Yearly discharge flux is the total water-year discharge/area. Yearly runoff ratio is the discharge flux/precipitation flux.
[a] Data not available.
[b] MFC-660 was ungauged un July–September of 2007. The runoff contribution for that period was very small and its omission negligibly affects the results.

Table II.

| Gauging station (USGS ID) | Drainage area (ha) | Period of historical data | Average watershed precipitation (mm) | Average discharge flux (mm/year) | Average runoff ratio |
|---|---|---|---|---|---|
| **Missouri Flat Creek at Pullman (13 348 500)** | 7019 | 1934–1979 | 533 | 108 | 0.20 |
| **SF Palouse River at Pullman (13 348 000)** | 34 188 | 1935–1980 | 559 | 103 | 0.18 |
| **Palouse River at Hooper (13 351 000)** | 647 497 | 1898–1979 | 457 | 85 | 0.19 |

Historical gauging data collected by the USGS at three stations within the Palouse River Watershed (Williams and Person, 1985).

were not seen at MFC-5700, occurred in June 2001, April, 2003, August 2005, and July 2007, with $\delta^{18}O$ values reaching −6·6‰, −5·1‰, −4·8‰, and −8·2‰, respectively. Winter $\delta^{18}O$ values consistently dipped to approximately −14·5‰ for most years. Two extreme $^{18}O$ depletion events occurred in January/February 2002 and January 2004, with $\delta^{18}O$ values reaching −17·4‰ and −18·6‰, respectively for MFC-4700 and −16·9‰ and −17·8‰ for MFC-5700. These $^{18}O$ depletion events coincided with the depletion events noted above at ES-6, TD-12, and MFC-660, as well as with highly $^{18}O$ depleted precipitation at that time.

Soil water in shallow lysimeters (Figure 5C) had a more rapid, high-amplitude isotopic response to precipitation inputs than deeper lysimeters, and TD-12 $\delta^{18}O$ values during some peak flows reflected a shallow soil water input to tile drainage. However, this shallow water signal appeared to be short-lived where sampling frequency was sufficient to test this (e.g. December 2003–January 2004).

*Electrical conductivity of MFC waters*

In uncontaminated water samples, measured EC is a good proxy for ionic load, mineral—water interaction time, and flow pathway (Freeze and Cherry, 1979). Because dissolved agricultural nitrate and its counterions ($K^+$ and $Ca^{2+}$) can increase EC measurements by as much as 30% during intervals of high nitrate concentration, the effect of this contamination is subtracted out of measured values using the procedure of Keller *et al.* (2008) documented by Simmons (2003) and Wannamaker (2005). The term 'EC' will henceforth refer to EC values corrected for nitrate contamination by this procedure. EC was measured to be near 0 μS cm$^{-1}$ for most precipitation samples. However, occasional samples did have detectable EC that may represent contamination of rain droplets in summer as a result of throughfall to the rain collector (via tall grass interception), or settling of dust particles during summer harvest that accumulated in the rain collector and interacted with slightly acidic rainwater in the funnel and Nalgene® bottle. TD-12 and MFC-660

Table III.

| Sample site | Average winter d$^{18}$O (permil) | SD | Average summer d$^{18}$O (permil) | SD | Average d$^{18}$O (permil) for site | SD | Average winter EC (μS/cm) | SD | Average summer EC (μS/cm) | SD |
|---|---|---|---|---|---|---|---|---|---|---|
| **ES-6** | −15.4 | 1.9 | −13.3 | 1.2 | −14.8 | 1.9 | 130 | 124 | 223 | 56 |
| **ES-106** | −15.1 | 1.8 | −13.1 | 1.5 | −14.4 | 1.9 | 135 | 110 | 249 | 42 |
| **TD-12** | −14.8 | 0.7 | −14.6 | 1.2 | −14.7 | 0.9 | 205 | 81 | 240 | 26 |
| **MFC-660** | −14.5 | 1.8 | −14.3 | 0.7 | −14.4 | 1.4 | 199 | 96 | 257 | 39 |
| **MFC-4700** | −14.5 | 3.1 | −12.6 | 2.2 | −13.6 | 2.9 | 217 | 93 | 318 | 55 |
| **MFC-5700** | −13.9 | 1.4 | −14.4 | 1.4 | −13.2 | 1.2 | 249 | 116 | 662 | 82 |
| **Surficial groundwater**[a] | — | — | — | — | −14.7 | 0.7 | — | — | — | — |
| **Wanapum groundwater**[a] | — | — | — | — | −15.2 | 0.3 | — | — | — | — |

Seasonal-volume weighted d$^{18}$O for precipitation and sampling sites from 2000 to 2007. All d$^{18}$O values are relative to VSMOW. Winter months are from October 1 to March 31 and summer months are from April 1 to September 30.
[a] Data are from Larson *et al.*, 2000.

discharge EC showed definite seasonality with an average EC of 240 μS cm$^{-1}$ in summer and an average of 205 μS cm$^{-1}$ during the winter (Figure 3, Table III). In the relatively wet years of 2001–2002, 2003–2004, and 2006–2007, the winter EC 'trough' value was ∼100 μS cm$^{-1}$ (Figure 3). Keller *et al.* (2008) hypothesized that lower TD-12 EC in the winter was the result of mobilized shallow pore water mixing with deeper profile waters, while higher EC in the summer was dominantly deeper soil water.

Surface waters at MFC-4700 and MFC-5700 show greater seasonal EC variability than those at TD-12 and MFC-660, with average summer EC of 375 μS cm$^{-1}$ and 480 μS cm$^{-1}$ for MFC-4700 and MFC-5700 waters, respectively, while the average winter EC was 200 μS cm$^{-1}$ for both MFC-4700 and MFC-5700 waters (Table III and Figure 4). The winter EC 'troughs' were similar to those exhibited by TD-12 and MFC-660. MFC-5700 waters exhibited EC values that were slightly higher than EC for MFC-4700 waters for the same sample date.

## DISCUSSION

*Precipitation δ$^{18}$O input to soil water and resulting δ$^{18}$O composition of streamflow*

An arresting aspect of our data is the consistency of δ$^{18}$O values in discharge from TD-12 and MFC-660 over the study period (Figures 3 and 5A). With highly seasonal δ$^{18}$O values for precipitation inputs to soil, it might be expected that TD-12 discharge would follow seasonal trends if simple piston flow were the primary mechanism of soil water transport from surface to tile drain. This is not the case, and average TD-12 discharge is isotopically indistinguishable from winter precipitation (Figure 6). Therefore, winter precipitation seems to control the field scale, deep soil water isotopic signature represented by TD-12, while summer precipitation has little if any influence. Our TD-12 discharge is isotopically very similar to the shallowest groundwater values found by Larson *et al.* (2000), who reported an average δ$^{18}$O value of −14·5‰ for groundwater in loess on the Palouse.

The stability of TD-12 δ$^{18}$O values throughout the year is probably attributable to summer precipitation that does not reach drain depth, and smoothing of winter precipitation δ$^{18}$O variability due to mixing in the soil profile. Soil water content from shallow to middle depths reached minimum values during summer (Figure 5B) and lysimeters were unable to collect pore waters at these times (Figure 5A). It can be concluded that summer precipitation was 'filtered out' of drainage as any summer precipitation that infiltrated the soil was taken up by plants and transpired. Conversely, winter precipitation that infiltrated the soil mixed with deeper pore water and variability in precipitation δ$^{18}$O values was averaged, except during high-flow events (Figure 5A). This mixing of winter precipitation reduced TD-12 δ$^{18}$O seasonality, and as a result 'old' and 'new' water contributions to tile drainage were largely indistinguishable on the timescale of this study.

Seasonal variability of TD-12 EC indicates seasonally different mean residence times among isotopically indistinguishable waters. Observed lower EC in winter TD-12 discharge (Figure 3, Table III) can be understood as a combination of shallow and deep-water inputs. These results differ from findings by Shanley *et al.* (2002) who observed that during peak meltwater discharge, lower EC coincided with the lowest δ$^{18}$O values at their agricultural site. One of the hypotheses proposed by Shanley *et al.* (2002) to explain this behavior was that tile drainage lowered the water table and therefore limited the storage of 'old' water, which consequently decreased the 'old' water contribution while passing more seasonal precipitation variability more directly to stream water. By contrast at TD-12, seasonal variability in δ$^{18}$O values is all but absent due to the filtering and mixing effects of a relatively deep, high water-storage drainage pathway.

In discharge from MFC-660 and TD-12, there were a few isolated cases where high flow was associated with lower EC and δ$^{18}$O values similar to the results found at the agricultural site in the Sleepers River study (Shanley *et al.*, 2002). In January 2004, the isotopic composition of the TD-12 discharge (−16·4‰, Figure 5A) was close to the monthly volume-weighted δ$^{18}$O for precipitation in
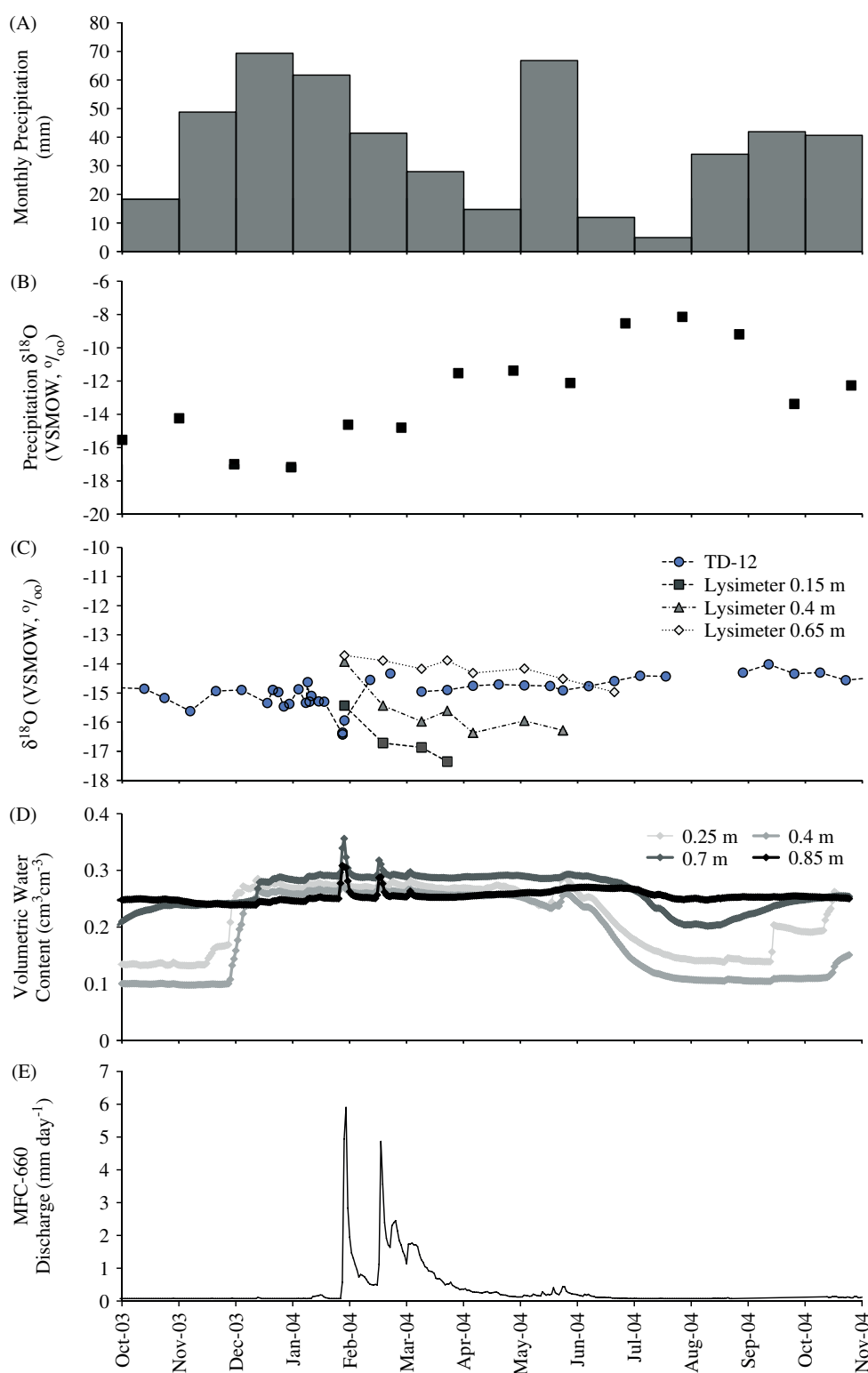
Figure 5. Soil water dynamics at TD-12 sampling location from Oct 2003 to Nov 2004. (A) Monthly precipitation, (B) Monthly volume weighted precipitation $\delta^{18}O$ values, (C) TD-12 and lysimeter $\delta^{18}O$ values, (D) volumetric water content (measured by TDR, from Keller *et al*., 2008), and (E) MFC-660 discharge

January 2004 ($-17 \cdot 2‰$). Additionally, the relatively stable soil water content at depth (85 cm) was also affected by this period of high flow (Figure 5B). However, these occurrences are probably attributable to preferential flow pathways and were not typical or recurring events for the MFC watershed over this 7-year study period. The event

that occurred in January 2004 had a short-term impact on soil water dynamics, but it did not have lasting effects on water chemistry for the following year.

During high flow events, MFC-660 $\delta^{18}O$ tended to track $\delta^{18}O$ values for ES-6 (e.g. during winters of 2003 and 2004; Figure 3), and these events coincided with high
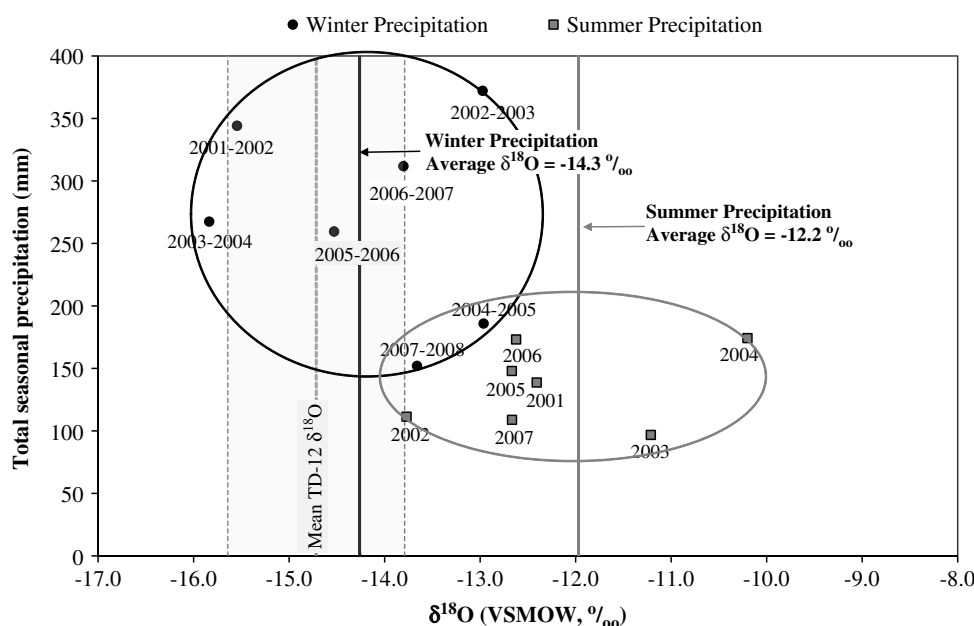
Figure 6. Seasonally weighted precipitation $\delta^{18}$O (summer: April—September; winter: October - March). Average winter precipitation $\delta^{18}$O was within one standard deviation of the $-14.7‰$ (SD $0.92‰$) $\delta^{18}$O baseline found at TD-12 (represented by gray vertical bar)

or low monthly volume-weighted winter precipitation $\delta^{18}$O at those times (compare with Figure 2). The close relationship of ES-6 and MFC-660 during events suggests that surface runoff may have occurred during high flow especially in non-tile drained fields, as hypothesized by Simmons (2003).

Keller *et al*. (2008) put forth a conceptual framework that stated that streamflow generation was primarily from discharge of soil water, and increased discharge in winter was due predominantly to rapid lateral flow of shallower soil water after soil water content was sufficiently high. This was supported by observed seasonal variability of EC in TD-12 and MFC-660, interpreted to indicate long (and deep) flowpaths during summer, on which were superposed shorter (and shallower) flowpaths in winter. A stable $\delta^{18}$O baseline of $-14.7‰$ for TD-12 and MFC-660 discharge is not inconsistent with this conceptual framework, but rather highlights the fact that isotopically 'new' and 'old' waters in discharge were not distinguishable in this dataset except during occasional events. These relationships are shown schematically in Figure 7. These ideas are consistent with other studies in which streamflow was generated via soil wetting and lateral flow along with occasional overland-flow events rather than a bedrock source (Kvaerner and Klove, 2006, 2008)

*Role of evaporation in isotope-geochemical evolution of stream water*

Winter $\delta^{18}$O values for surface waters at all catchment scales were consistent from year to year, with mean winter $\delta^{18}$O values closely matching the isotopic signature of mean TD-12 discharge (Figures 3 and 4; Table III). Superimposed upon this steady signal are the signatures (e.g. ES-6) of occasional events, observed at MFC-660 and propagated down the watershed; and the rhythmic

summer-season $^{18}$O enrichment excursions observed at MFC-4700 and MFC-5700 (Figure 4). These observations are consistent with a conceptual framework in which soil water seepage via tile drains or directly to ditches (Figure 7), originating as winter precipitation and occasionally augmented by overland-flow events, is the dominant source of streamflow generation in the MFC watershed; and some other process or source modifies the fundamental $\delta^{18}$O signature during low flow at large catchment scales. Simmons (2003), observing high EC at MFC-4700 during the summer, envisioned groundwater from shallow basalts as a primary component of downstream surface waters during low flow. If this were the case, the $\delta^{18}$O value of this shallow basalt component would have to be from $-12‰$ to $-11‰$ or higher according to observed summer $\delta^{18}$O values at MFC-4700 (Figure 4). However, Larson *et al*. (2000) found considerably lower $\delta^{18}$O values in basalt groundwater ($-15.2‰$ SD $0.3‰$in the shallow aquifer and $-16.7‰$ SD $0.6‰$in the deeper aquifer).

Figure 4 further illustrates how $\delta^{18}$O and EC values for MFC-4700 and MFC-5700 were rhythmically and synoptically enriched compared to those of the discharge from TD-12. We hypothesize that this was due to direct evaporation from the stream water surface. The extent of evaporation was roughly estimated by two independent evaporation indices, $E/I_{\delta^{18}O}$ (Equation 9) and $E/I_{EC}$ (Equation 10). Estimates for $E/I_{\delta^{18}O}$ for MFC-5700 show significant evaporative loss from August to October after harvest, with $E/I_{^{18}O}$ ranging between 25% and 35% from 2001 to 2007. MFC-4700 $E/I_{^{18}O}$ values ranged from 14% to 45%. For the same time periods, $E/I_{EC}$ for both MFC-4700 and MFC-5700 ranged between 30% and 40%. The similarity of evaporative loss estimated by these two independent methods supports the hypothesis that
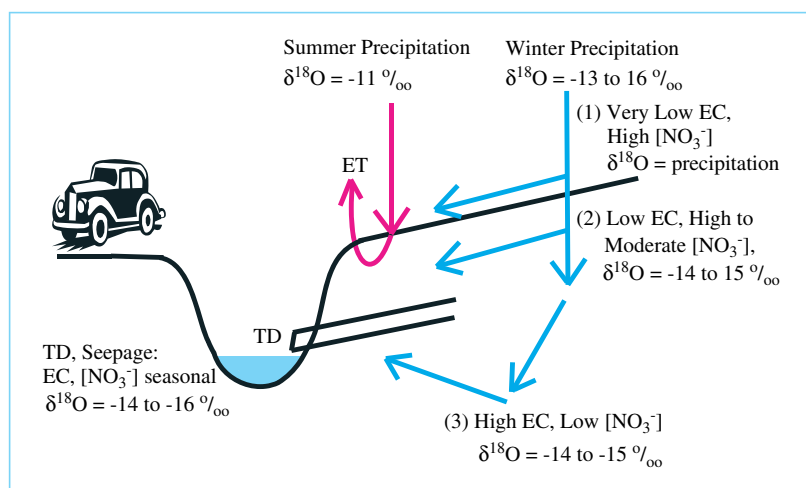
Figure 7. Conceptual model of flow pathways generating streamflow in the MFC. Summer precipitation is nearly all evaporated or transpired and does not appreciably contribute to streamflow. Streamflow is generated by winter precipitation and can be partitioned into three components: (1) Storm/melt runoff, (2) shallow lateral flow, and (3) deeper percolation contributing to sustained TD-12 flow and soil seepage. Nitrate concentration $[NO_3^-]$ trends summarized from Keller *et al.* (2008)

$^{18}$O enrichment observed at MFC-4700 and MFC-5700 was due to evaporative enrichment of surface water in summer, and does not reflect differing proportions of 'old' and 'new' water. Gibson *et al.* (1993) found that evaporative flux made up 7–19% of total discharge for two lakes in northern Canada, and 40% evaporation in the upper reaches of a dryland river in Australia (Gibson *et al.*, 2008).

The isotopic results of our study seem to be in contrast with the results of most previous isotope-hydrologic watershed studies. Summer precipitation did not affect the isotopic composition of MFC stream water as it did in watersheds at Hubbard Brook (Hooper and Shoemaker, 1986), Sleepers River (Shanley *et al.*, 2002), Panola (Hooper *et al.*, 1990), or La Selva Biological Station in Costa Rica (Genereux *et al.*, 2002, 2004, 2006). Hooper and Shoemaker (1986) observed strong depletion events in stream waters as a result of spring snowmelt at Hubbard Brook, which were observed as excursions in TD-12 and MFC waters during Jan-Feb 2004. Genereux *et al.* (2002, 2004, 2006) observed two distinctive sources of groundwater in stream waters in Costa Rica. By contrast, it seems clear that soil water, and shallow groundwater drained by drain tiles in the summer, were the principal sources of streamflow generation in the MFC watershed, and that evaporation (summer) and occasional events (winter) were the principal sources of isotopic variation in stream water. Our observed stream systematics are similar to summer isotope enrichment trends observed in dryland stream channels in Australia (Gibson *et al.*, 2008) and summer isotope enrichment in rivers in Florida (Gremillion and Wanielista, 2000). Event-based monitoring could resolve the contributions of shallow and deep pore waters during these events (e.g. Simmons, 2003). However, the stability of the TD-12 and MFC-660 isotopic records is a key feature of the isotope hydrology of this watershed. The superposed effect of evaporation on EC and $\delta^{18}$O values in surface waters increases the complexity of defining end-members in hydrograph separations.

*Implications for streamflow generation and shallow groundwater recharge in the Palouse region*

The isotopic composition at the Palouse River Watershed USGS gauging station at Hooper from 2000 to 2001 (Figure 8) showed strongly seasonal fluctuations with enriched $\delta^{18}$O values in the summer ($\sim -11‰$) and depleted $\delta^{18}$O during the winter ($\sim -14·5‰$). At the same site, EC (non-nitrate corrected) from 1999 to 2004 showed seasonal variability with values peaking during low flow (maximum summer EC of 380 µS cm$^{-1}$) and dipping to low levels during high flow (minimum winter EC from 125 to 175 µS cm$^{-1}$). This seasonal variation for the Hooper gauging station, located 96 km west of the MFC (Figure 1) and representing more than 100 times the area of our largest catchment, is similar to observed isotopic and EC seasonality at MFC-4700 and MFC-5700. In addition, historic data collected from 1898 to 1979 at the Palouse River gauging station at Hooper, WA (Williams and Pearson, 1985), provided a consistent runoff ratio of 0·2 (Table II). This indicates that the MFC watershed, and mechanisms of streamflow generation (Figure 7) and surface hydrologic dynamics, may be typical of other larger agricultural watersheds in the Palouse region.

Larson *et al.* (2000) suggested that shallow basalt ground water was recharged by recent precipitation (within the past 10–100 years). They reported that shallow groundwater in the Wanapum aquifer had mean $\delta^{18}$O composition of $-15·2‰$, which was statistically indistinguishable from groundwater in loess with a mean $\delta^{18}$O composition of $-14·5‰$. These values are close to those of mean winter precipitation (Figure 6, Table III) and mean wintertime streamflow (Figures 3 and 4, Table III). Taken together, these results indicate that winter precipitation is probably the source of both surface and groundwater in this region.
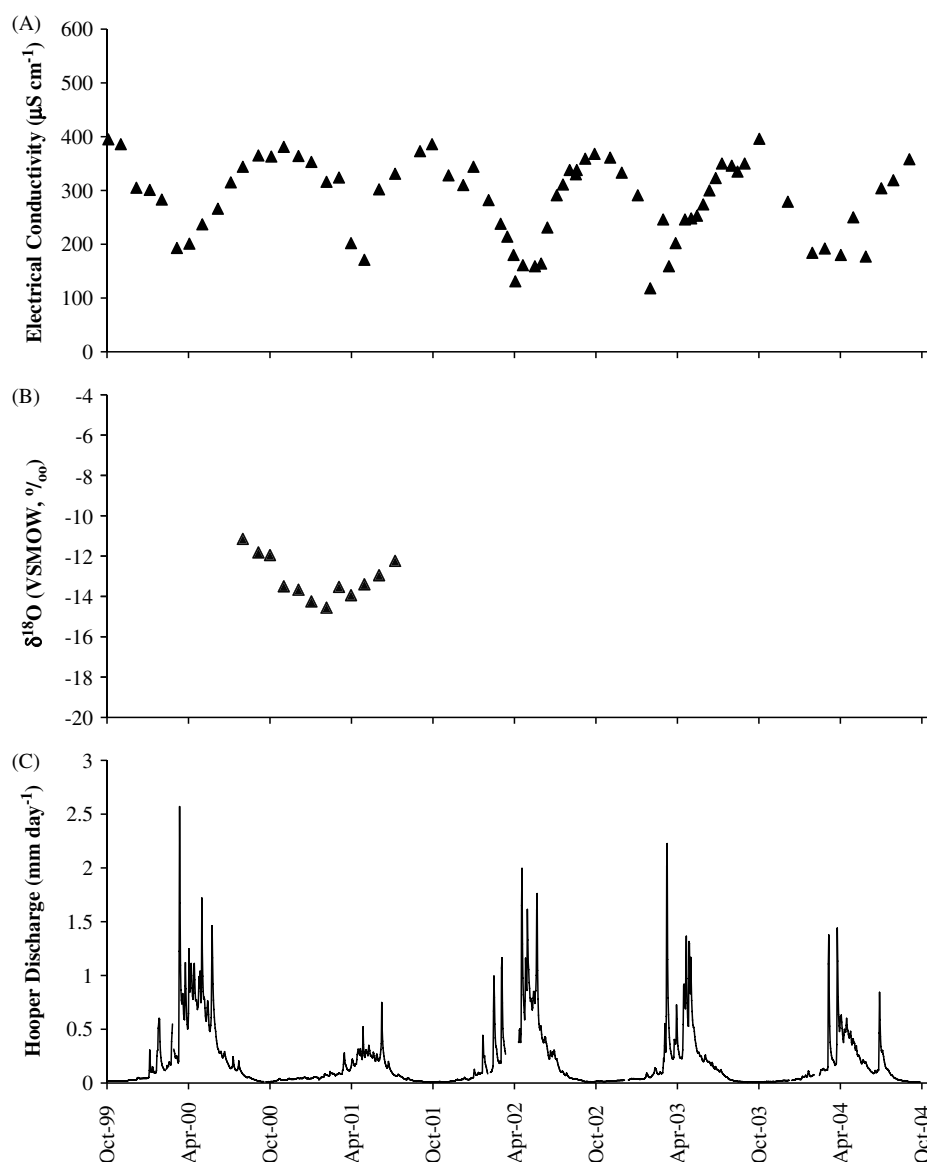
Figure 8. EC (A), $\delta^{18}O$ (B), and discharge (C) (USGS data) dynamics observed in waters collected at the Palouse River gauging station at Hooper, WA. $\delta^{18}O$ and EC dynamics observed at both MFC-4700 and MFC-5700 in the MFC watershed were similar to those at Hooper

There appears to be a slight overall enrichment trend in $\delta^{18}O$ for TD-12 and MFC-660 discharge from 2000–2007 (Figure 3), which cannot be attributed to errors. A simple linear regression of TD-12 $\delta^{18}O$ values vs. time in Figure 3B shows a positive linear increase in $\delta^{18}O$ values from 2000 to 2008 ($\delta^{18}O_{TD-12} = -15.17 + (3.4 \times 10^{-4}) \times day$, $R^2 = 0.13$, $F = 27.5$, $p < 0.0001$). Although slight, this decadal trend towards higher $\delta^{18}O$ values could be a result of increased average temperatures for the Palouse. Assuming that the discharge $\delta^{18}O$ trends straightforwardly transmit precipitation $\delta^{18}O$ trends over this period, and using the global precipitation isotope-temperature relationship from Dansgaard (1964), the estimated temperature increase that could account for the slight enrichment of TD-12 $\delta^{18}O$ is $1.3 \pm 0.5\,°C$. Alternatively, a gradual increase in baseline $\delta^{18}O$ at TD-12 may be the result of recurring El Niño/Southern Oscillation events over the past decade (Jacobs *et al.*, 1994). However, El Niño events are short-lived (persistence of

6–18 months) and have primary effects on climate in the southwestern United States and the tropics (Andrade and Sellers, 1988), with only secondary effects in the northwestern US. The more likely cause for the gradual enrichment of $\delta^{18}O$ in MFC soil waters may be the Pacific Decadal Oscillation (PDO), which has been shown to have primary and sustained effects (cycles of 20 years) on the climate of the northwestern US and Canada (Kitzberger *et al.*, 2007). For the past decade, the PDO has exhibited a warming phase that has been marked by warmer coastal waters off of Washington and British Columbia, a colder Pacific Ocean north of 20°N (http://jisao.washington.edu/pdo/, accessed April 2008), a higher incidence of forest fires (Kitzberger *et al.*, 2007), and climatic changes in the western US (Benson *et al.*, 2003). The warm coastal waters and increased spring-time temperatures may affect the isotopic dynamics of late winter precipitation with less rainout and less depletion of residual vapor masses that precipitate over the

Palouse, which may produce changes in precipitation or evapotranspiration patterns.

## CONCLUSIONS AND IMPLICATIONS

Isotopic data collected in tile drainage and nested catchments from 2000 to 2008 showed that winter precipitation was the primary source of streamflow and shallow groundwater recharge in the MFC watershed. $\delta^{18}O$ values for groundwater collected in loess and the shallow basalt-aquifer were statistically indistinguishable from those in our small-catchments, suggesting that recharge to these systems could be from recent winter precipitation. This suggests that contamination of the shallow basalt-aquifer could occur as agrochemicals have been shown to mobilize during high flow in winter (Keller *et al.*, 2008).

The isotopic seasonality of stream waters in the MFC watershed was likely due to in-stream evaporation at larger catchment scales, and does not represent a separate basalt groundwater source in this watershed. Identification of seasonally-variable 'new' and 'old' water contributions to TD-12 and MFC-660 discharges was not possible using $\delta^{18}O$ end-member mixing models, because soil water seepage and tile drainage to ditches throughout the year were generated by infiltration and mixing of winter precipitation. Seasonal trends of EC from both TD-12 and MFC-660 suggest that short, shallow subsurface pathways contributed to winter stream water generation and long, deep subsurface pathways dominated summer stream waters. Events that rapidly changed water chemistry and isotopes were occasionally important to stream water dynamics in the MFC watershed.

Isotope systematics for the MFC appears to be characteristic of the larger Palouse River watershed. A slight long-term enrichment trend in our tile drain data, and the enrichment of seasonally volume-weighted precipitation $\delta^{18}O$ over the past decade, suggest that decadal-scale climatic changes, such as PDO, may have impacted the hydrology of the region.

## ACKNOWLEDGEMENTS

## REFERENCES

Abdou HM. 2003. *Modeling pesticide leaching at field-to-regional scale using an integrated GIS/solute transport approach*. Dissertation. Washington State University, Pullman, WA.

Andrade ER, Sellers WD. 1988. El Nino and its effects on precipitation in Arizona and Western New Mexico. *Journal of Climatology* **8**(4): 403–410.

Barnes CJ, Allison GB. 1983. The distribution of deuterium and $^{18}O$ in dry soils, 1. Theory. *Journal of Hydrology* **60**: 141–156.

Barnes CJ, Allison GB. 1984. The distribution of deuterium and $^{18}O$ in dry soils 3. Theory for non isothermal water movement. *Journal of Hydrology* **74**: 119–135.

Barnes CJ, Allison GB. 1988. Tracing of water movement in the unsaturated zone using stable isotopes of hydrogen and oxygen. *Journal of Hydrology* **100**: 143–176.

Benson L, Linsley B, Smoot J, Mensing S, Lund S, Stine S, Sarna-Wojcicki A. 2003. Influence of the Pacific Decadal Oscillation on the climate of the Sierra Nevada, California and Nevada. *Quaternary Research* **59**: 151–159.

Bottinga Y, Craig H. 1969. Oxygen isotope fractionation between $CO_2$ and water, and the isotopic composition of marine atmosphere. *Earth and Planet Science Letter* **5**: 285–295.

Bottinga Y, Javoy M. 1973. Comments on oxygen isotope geothermometry. *Earth and Planet Science* **20**: 250–265.

Brooks E, Yao C, Boll J, Chen S, McCool D. 2006. Improving tillage systems for minimizing erosion, STEEP Final Project Report [Online]. Available at http://pnwsteep.wsu.edu/annualreports/2006/pdf/Boll_Impr_Tillage.pdf (verified 19 Apr. 2007). Solutions to Environmental and Economic Problems, Washington State University/Oregon State University/University of Idaho.

Cambardella CA, Moorman TB, Jaynes DB, Hatfield JL, Parkin TB, Simpkins WW, Karlen DL. 1999. Water quality in Walnut Creek watershed: Nitrate- nitrogen in soils, subsurface drainage water, and shallow groundwater. *Journal of Environmental Quality* **28**: 25–34.

Carey SK, Quinton WL. 2005. Evaluating runoff generation during summer using hydrometric, stable isotope and hydrochemical methods in a discontinuous permafrost alpine catchment. *Hydrological Processes* **19**: 95–114.

Craig H. 1961. Isotopic variations in meteoric waters. *Science* **133**: 1702–1703.

Craig H, Gordon LI. 1965. Deuterium and oxygen-18 variations in the ocean and marine atmosphere. In *Proceedings Conference. Stable Isotopes in Oceanography Studies and Paleotemperatures*. Laboratory of Geology and Nuclear: Pisa, 9–130.

Dansgaard W. 1964. Stable isotopes in precipitation. *Tellus* **16**: 436–468.

DePaolo DJ, Conrad ME, Maher K, Gee GW. 2004. Evaporation effects on oxygen and hydrogen isotopes in deep vadose zone pore fluids at Hanford, Washington. *Vadose Zone Journal* **3**: 220–232.

Donaldson NC. 1980. *Soil survey of Whitman County, Washington. USDA—Soil Conservation Service*. Washington State University—Agricultural Research Center: Washington.

Douglas AA, Osiensky JL, Keller CK. 2007. Carbon-14 dating of ground water in the Palouse Basin of the Columbia River basalts. *Journal of Hydrology* **334**: 502–512.

Endreny TA. 2002. Forest buffer strips: Mapping the water quality benefits. *Journal of Forestry* **100**(1): 35–40.

Epstein S, Mayeda TK. 1953. Variation of $^{18}O$ content of waters from natural sources. *Geochimica et Cosmochimica Acta* **4**(5): 213–224.

Freeze RA, Cherry JA. 1979. *Groundwater*. Prentice Hall, Inc.: Upper Saddle River, NJ; 604.

Gat JR. 1996. Oxygen and hydrogen isotopes in the hydrologic cycle. *Annual Review of Earth and Planetary Sciences* **24**: 225–262.

Gat JR, Levy Y. 1978. Isotope hydrology of inland sabkhas in the Bardawil area, Sinai. *Limnology and Oceanography* **25**(5): 841–850.

Gat JR, Gonfiantini R. 1981. Stable isotope hydrology. Deuterium and oxygen-18 in the water cycle. Technical Reports Series No. 210, (23B INT). International Atomic Energy Agency: Vienna, 347.

Gburek WJ, Folmer GJ. 1999. Flow and chemical contributions to streamflow in an upland watershed: a baseflow survey. *Journal of Hydrology* **217**: 1–18.

Genereux DP. 2004. Comparison of naturally-occurring chloride and oxygen-18 as tracers of interbasin groundwater transfer in lowland rainforest, Costa Rica. *Journal of Hydrology* **295**: 17–27.

Genereux DP, Hooper RP. 1998. Oxygen and hydrogen isotopes in rainfall-runoff studies. In *Isotope Tracers in Catchment Hydrology*, Kendall C, McDonnell JJ (eds). Elsevier Science B.V.: Amsterdam; 319–346.

Genereux DP, Jordan M. 2006. Interbasin groundwater flow and groundwater interaction with surface water in a lowland rainforest, Costa Rica: a review. *Journal of Hydrology* **320**: 385–399.

Genereux DP, Wood SJ, Pringle CM. 2002. Chemical tracing of interbasin groundwater transfer in the lowland rainforest of Costa Rica. *Journal of Hydrology* **258**: 163–178.

Geyer DJ, Keller CK, Smith JL, Johnstone DL. 1992. Subsurface fate of nitrate as a function of depth and landscape position in Missouri Flat Creek Watershed: Setting and farming practices. *Journal of Environmental Quality* **28**: 11–24.

Gibson JJ. 2001. Forest-tundra water balance signals traces by isotopic enrichment in lakes. *Journal of Hydrology* **251**: 1–13.

Gibson JJ. 2002. Short term evaporation and water budget comparisons in shallow Arctic lakes using non-steady isotope mass balance. *Journal of Hydrology* **264**(1–4): 242–261.

Gibson JJ, Edwards TWD, Birks SJ, St Amour NA, Buhay WM, McEachern P, Wolfe BB, Peters DL. 2005. Progress in isotope tracer hydrology in Canada. *Hydrological Processes* **19**: 303–327.

Gibson JJ, Edwards TWD, Bursey GG. 1993. Estimating evaporation using stable isotopes: Quantitative results and sensitivity analysis fro two catchments in Northern Canada. *Nordic Hydrology* **24**: 79–94.

Gibson JJ, Prepas EE, McEachern P. 2002. Quantitative comparison of lake throughflow, residency, and catchment runoff using stable isotopes: modeling and results from a regional survey of Boreal lakes. *Journal of Hydrology* **262**: 128–144.

Gibson JJ, Price JS, Aravena R, Fitzgerald DF, Maloney D. 2000. Runoff generation in a hypermaritime bog-forest upland. *Hydrological Processes* **14**: 2711–2730.

Gibson JJ, Reid R, Spence C. 1998. A six-year isotopic record of lake evaporation at a site in the Canadian subarctic: results and validation. *Hydrological Processes* **12**: 1779–1792.

Gibson JJ, Sadek MA, Stone DJM, Hughes CE, Hankin S, Cendon DI, Hollins SE. 2008. Evaporative isotope enrichment as a constraint on reach water balance along a dryland river. *Isotopes in Environmental and Health Studies* **44**(1): 83–98.

Goodwin AJ. 2006. *Oxygen-18 in surface and soil waters in a dryland agricultural setting, Eastern Washington: flow processes and mean residence times at various watershed scales*. Thesis, Washington State University, Pullman, WA.

Gremillion P, Wanielista M. 2000. Effects of evaporative enrichment on the stable isotope hydrology of a central Florida (USA) river. *Hydrological Processes* **14**(8): 1465–1484.

Hooper RP, Shoemaker CH. 1986. A comparison of chemical and isotopic hydrograph separation. *Water Resources Research* **22**(10): 1444–1454.

Hooper RP, Christopherson N, Peters NE. 1990. Modelling streamwater chemistry as a mixture of soilwater end-members—an application to Panola Mountain catchment, Georgia, USA. *Journal of Hydrology* **116**(1–4): 321–343.

Horita J, Wesolowski DJ. 1994. Liquid-vapor fractionation of oxygen and hydrogen isptopes of water from the freezing to the critical temperatures. *Geochimica et Cosmochimica Acta* **58**(16): 3425–3427.

Jacobs GA, Hurlburt HE, Kindle JC, Metzger EJ, Mitchell JL, Teague WJ, Wallcraft AJ. 1994. Decade-scale trans-Pacific propagation and warming effects of an El Nino anomaly. *Nature* **370**: 360–363.

Keller CK, Butcher CN, Smith JL, Allen-King RM. 2008. Nitrate in tile drainage of the semi-arid palouse basin. *Journal of Environmental Quality* **37**: 353–361.

Kendall C, McDonnell JJ (eds). 1998. *Isotope Tracers in Catchment Hydrology*. Elsevier Science B.V.: Amsterdam, The Netherlands; 839.

Kitzberger T, Brown PM, Heyerdahl EK, Swetnam TW, Veblen TT. 2007. Contingent Pacific-Atlantic Ocean influence on multicentury wildfire synchrony over western North America. *Proceedings of the National Academy of Sciences of the United States of America* **104**(2): 543–548.

Kladivko EJ, van Scoyoc GE, Monke EJ, Oates KM, Pask W. 1991. Pesticides and nutrient movement into subsurface tile drains on a silt loam soil in Indiana. *Journal of Environmental Quality* **20**: 264–270.

Kvaerner J, Klove B. 2006. Tracing sources of summer streamflow in boreal headwaters using isotopic signatures and water geochemical components. *Journal of Hydrology* **331**(1–2): 186–204.

Kvaerner J, Klove B. 2008. Generation and regulation of summer runoff in a boreal flat fen. *Journal of Hydrology* **360**(1–4): 15–30.

Larson KR, Keller CK, Larson PB, Allen-King RM. 2000. Water resource implications of $^{18}O$ and $^2H$ distributions in a basalt aquifer system. *Groundwater* **38**: 947–953.

Laudon H, Slaymaker O. 1997. Hydrograph separation using stable isotopes, silica, and electrical conductivity: an alpine example. *Journal of Hydrology* **201**: 82–101.

Lum WE, Smoot JL, Ralston DR. 1990. Geohydrology and numerical model analysis of ground-water flow in the Pullman–Moscow area, Washington and Idaho. U.S. Geological Survey Water-Resources Investigations Report, 89–4103.

Mallawatantri AP, McConkey BG, Mulla DJ. 1996. Characterization of pesticide sorption and degradation in macropore linings and soil horizons of Thatuna silt loam. *Journal of Environmental Quality* **25**: 227–235.

Marimuthu S, Reynolds DA, Le Gal La Salle C. 2005. A field study of hydraulic, geochemical and stable isotope relationships in a coastal wetlands system. *Journal of Hydrology* **325**: 93–116.

McDonald EV, Busacca AJ. 1992. Late Quaternary stratigraphy of loess in the Channeled Scabland and Palouse regions of Washington State. *Quaternary Research* **38**: 141–156.

O'Geen AT, McDaniel PA, Boll J, Keller CK. 2005. Paleosols as deep regolith: Implications for ground-water recharge across a loessial climosequence. *Geoderma* **126**: 85–99.

Peters NE, Ratcliffe EB. 1998. Tracing hydrologic pathways using chloride at the Panola Mountain Research Watershed, Georgia, USA. *Water Air and Soil Pollution* **105**: 263–275.

Randall GW, Huggins DR, Russelle MP, Fuchs DJ, Nelson WW, Anderson JL. 1997. Nitrate losses through subsurface tile drainage in conservation reserve program, alfalfa and row crop system. *Journal of Environmental Quality* **26**: 1240–1247.

Shanley JB, Kendall C, Smith TE, Wolock DM, McDonnell JJ. 2002. Controls on old and new water contributions to stream flow at some nested catchments in Vermont, USA. *Hydrological Processes* **16**: 589–609.

Shelton LR. 1994. Field guide for collecting and processing stream-water samples for the National Water-Quality Assessment Program. Denver, CO, Sacramento, CA. U.S. Geological Survey.

Simmons A. 2003. *Dissolved pesticide mass discharge in a semi-arid dryland agricultural watershed at the field and basin scale*, Thesis. Washington State University, Pullman, WA.

Sklash MG, Farvolden RN. 1979. The roles of groundwater in storm runoff. *Journal of Hydrology* **43**: 45–65.

Sklash MG, Farvolden RN, Fritz P. 1976. A conceptual model of watershed response to rainfall developed through the use of oxygen-18 as a natural tracer. *Canadian Journal of Earth Sciences* **13**: 271–283.

Strauch G, Oyarzun J, Fiebig-Wittmaack M, Gonzalez M, Weise SM. 2006. Contributions of the different water sources to the Elqui river runoff (northern Chile) evaluatied by H/O isotopes. *Isotopes in Environmental and Health Studies* **42**(3): 303–322.

Takeuchi A, Goodwin AJ, Moravec BG, Larson PB, Keller CK. 2009. Isotopic evidence for temporal variation in proportion of seasonal precipitation since the last glacial time in the inland Pacific Northwest of the USA. *Quaternary Geology* **27**: 198–206.

USDA. 1978. *Palouse Cooperative River Basin Study*. SCS, Forest Service, and Economics, Statistics, and Cooperative Extension Service. U.S. Government Print: Washington, DC.

Walker CD, Brunel JP. 1990. Examining evapotranspiration in a semi-arid region using stable isotopes of hydrogen and oxygen. *Journal of Hydrology* **118**: 55–75.

Wannamaker C. 2005. *Edge of field nitrate occurrence and loss in a semi-arid dryland agricultural setting*. Thesis, Washington State University, Pullman, WA.

Williams JR, Pearson HE. 1985. Streamflow statistics and drainage-basin characteristics for the southwestern and eastern regions, Washington, Volume 2, Eastern Washington. *USGS Open File Report 84-145-B*, 662.

Winograd IJ, Riggs AC, Coplen TB. 1998. The relative contributions of summer and cool-season precipitation to groundwater recharge, Spring Mountains, Nevada, USA. *Hydrogeology Journal* **6**: 77–93.

Zimmermann U, Ehhalt D, Munnich KO. 1967. Soil-water movement and evapotranspiration: changes in the isotopic composition of the water. In *Proceedings of the Symposium of Isotopes in Hydrology, Vienna 1966*. IAEA: Vienna; 567–584.